



Tuning joint sequence for donor–acceptor polymers based on fluorinated benzothiadiazole with thiophene/furan bridged



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ABSTRACT

Three new donor–acceptor (D–A) polymers, PTBDT-ffBT-FT₁₂, PTBDT-ffBT-TT₁₂ and PTBDT-ffBT-T₁₂T, based on thiophene substituted benzene[1,2-b:4,5-b'] thiophene (TBDT) and fluorinated benzothiadiazole (ffBT) with thiophene/furan conjugated bridges were prepared. The joint sequence of alkyl thiophene/furan bridges has significant influence on the energy levels, band-gap and molecule stacking of the copolymers. All copolymers show broad absorption bands, and the energy level and band gap could be well fine-tuned by the introduction of thiophene/furan bridges to polymer backbone. The small atomic radius of oxygen atom on furan bridges resulted in the inferior co-planarity and torsion backbone for PTBDT-ffBT-FT₁₂ with furan bridges, while the adjacent dodecyl on thiophene bridges close to TBDT led to a big steric hindrance. As a result, the polymer solar cell (PSC) based on PTBDT-ffBT-T₁₂T achieves the better efficiency compared to PTBDT-ffBT-FT₁₂ and PTBDT-ffBT-TT₁₂.

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1. Introduction

Polymer solar cells (PSCs) are the promising alternative for clean and renewable energy because of their potential application in flexible, light-weight, and low-cost large-area devices through roll-to-roll printing [1–4]. Typically, p-type semiconductor (electron donor, such as conjugated polymers) and n-type semiconductor (electron acceptor, such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM)) are blended in a bulk heterojunction (BHJ) configuration as the core components for PSCs [5]. Although the photoelectric conversion efficiency (PCE) of BHJ polymer solar cells has reached 10% [6], the low PCE compared with that of inorganic solar cells limits its commercial production. The design and synthesis of new ideal polymers with narrow band-gap, broad absorption, high mobility and suitable energy levels is the most critical challenge at the molecular level to achieve high efficiency for PSCs. To broaden the response wavelength range of conjugated polymer and adjust the energy levels, one attractive approach is to construct donor–acceptor (D–A) conjugated polymers by alternating a conjugated electron-rich donor (D) unit and a conjugated electron-deficient acceptor (A) unit within the polymer backbone.

Furthermore, the introduction of π -extended fuse rings to D–A polymer backbone should be one of the most effective strategies to extend the length of π -conjugation and enhance strong intermolecular interactions between the neighboring polymer chains [7–13], which is beneficial for lower the energy band gap and improve the charge mobility. For example, compared with the original 2,1,3-benzothiadiazole (BT) unit, use two flanking thienyl units as the bridge rings in the di-2-thienyl-2,1,3-benzothiadiazole (DTBT) can relieve the severe steric hindrance between the BT unit and donor aromatic units (especially when benzene based aromatics are used) [14]. Thus, the synthesized D–A polymers adopt more planar structures to reduce the band gap by enhancing the D–A conjugation. In addition, the two electron-rich, flanking thienyl units would help to improve the hole mobility, since thiophene-based polymers have shown noticeably high hole mobility [15]. However, due to the electron-rich nature of these thienyl units, in some cases, the two flanking thienyl units would increase the highest occupied molecular orbital (HOMO) of the conjugated polymers when compared with BT-based polymers [16,17]. Strong electron-withdrawing fluorine atoms can be used as substituent to tune the HOMO and lowest unoccupied molecular orbital (LUMO) energy levels of D–A polymers and almost has no influence on the band-gap at the same time. You et al. has introduced two fluorine atoms into the commonly used BT unit, and transformed the BT into two fluorinated ffBT [18]. Compared with

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the polymer without fluorine atom, the polymer based on ffBT got lower HOMO and LUMO energy levels with the increased open circuit voltage (V_{oc}) of 0.91 V and PCE of 7.2%. Recently, Li et al. has also introduced a fluorine atoms into the BT unit, getting a polymer of P(BDT-TT-FBT) [19]. It is proved that the introduction of fluorine atom not only decreases the HOMO energy level, but also improves the intramolecular and intermolecular interaction, leading to the significantly increased V_{oc} and mobility. On the other hand, fine tuning the polymer structure by incorporating the bridge ring to the polymer backbone can further adjust the energy levels. For instance, replacing the thiophene by furan to the backbone will lower the HOMO level of polymer as the stronger electronegativity of oxygen atom than that of sulfur atom.

Herein, we choose the alkyl thiophene substituted benzene[1,2-b:4,5-b'] thiophene (TBDT), which has good co-planarity and high hole mobility, as the donor unit, and ffBT unit as the acceptor to design and synthesize new D–A conjugated polymers. In order to regulate the energy level and band gap of polymers, thiophene and furan bridge rings were introduced to the backbone of the conjugated polymers. Considering the impact of solubility and substitution position of alkyl chain to the energy level and morphology, dodecyl side chain was introduced to the different positions of bridge thiophene groups, obtaining three new D–A polymers: PTBDT-ffBT-FT₁₂ (furan as the bridge), PTBDT-ffBT-TT₁₂ (thiophene as the bridge) and PTBDT-ffBT-T₁₂T (thiophene as the bridge). The difference between PTBDT-ffBT-T₁₂T and PTBDT-ffBT-TT₁₂ was the position of alkyl chain connected to thiophene bridge groups. Photoelectric properties and morphology of these polymers have been studied, and the influence of joint sequence of alkyl thiophene

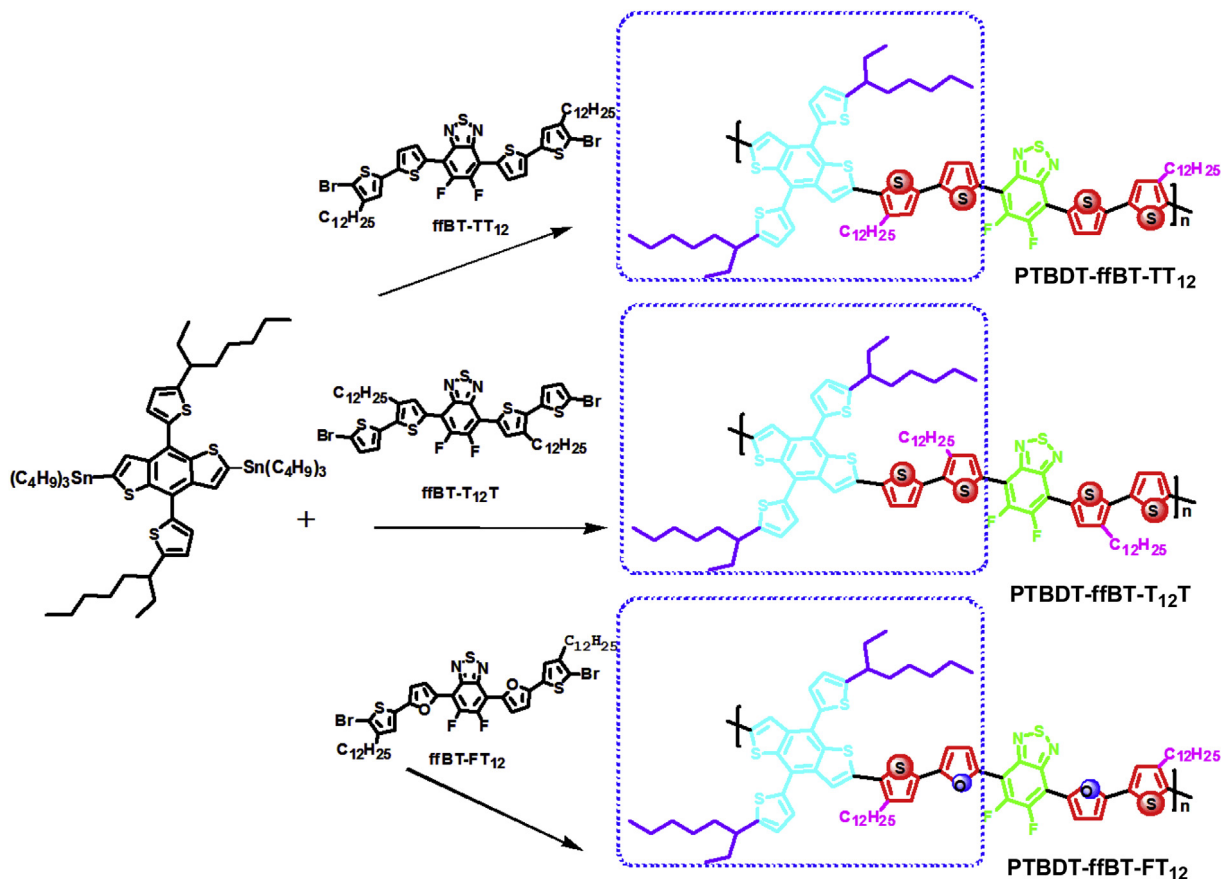
furan bridges on molecule level, band-gap and molecule stacking has also been investigated.

2. Results and discussion

Scheme 1 and Scheme S1 show the synthetic routes of three copolymers. The copolymers PTBDT-ffBT-T₁₂T, PTBDT-ffBT-TT₁₂ and PTBDT-ffBT-FT₁₂ were synthesized by Stille coupling polymerization using the same donor unit TBDT. Polymer PTBDT-ffBT-T₁₂T and PTBDT-ffBT-TT₁₂ have the similar backbones, just differ in the position of the dodecyl thiophene bridge. For the polymer PTBDT-ffBT-FT₁₂, thiophene bridge near the BT unit are replaced by furan ring compared with PTBDT-ffBT-TT₁₂, with the aim to study the influence of different aromatic bridges to the photoelectric of conjugated polymer backbone. The structures of the copolymers have been confirmed by NMR spectra, as revealed in Figure SI 1–6. The molecular weight (M_n and M_w) and polydispersity index (PDI) of the copolymers were obtained by performing gel permeation chromatography (GPC), and the related data are shown in Table S1. PTBDT-ffBT-FT₁₂ has a good solubility in chlorobenzene solution due to the low molecular weight, while PTBDT-ffBT-TT₁₂ and PTBDT-ffBT-T₁₂T shows relatively poor solubility in organic solvents, probably resulting from the existence of the F atom.

3. Thermal properties

Thermogravimetry analysis (TGA) of copolymers has been carried out to determine the thermal properties of the copolymers. Figure S7 shows the thermogravimetry analysis (TGA) of



Scheme 1. Synthetic routes for copolymers.

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